

5

POLYOL FORMULATION

FIELD OF THE INVENTION

10 **[0001]** The present invention relates to a
formulation for preparing high resilience foam
comprising a polyol formulation and to a process for
preparing high resilience polyurethane foam with a
polyol formulation.

BACKGROUND OF THE INVENTION

15 **[0002]** High resilience foams predominantly exhibit
elastic behavior, meaning that they change shape when
force is applied but return nearly instantaneously to
their initial shape when the applied force is
removed.

20 **[0003]** WO 03/016373 (not prepublished) relates to
the use of tertiary amine based polyol (b2iii) in a
copolymer composition (b2). The presence of the
tertiary amine polyol (b2iii) reduces and even
eliminates the need to include a conventional
25 tertiary amine and/or tin salt catalyst. Amine based
polyols (b2iii) are either initiated with a tertiary
amine compound or contain a tertiary amine group in
the polyol chain or are partially capped with a
tertiary amine group. Preferably, the tertiary amine
30 based polyol is 50 to 100% of the carrier polyol
present in (b2).

35 **[0004]** Although a wide range of different high
resilience foams are known, further foams are still
being developed in order to obtain specific
combinations of properties. It would be useful to
obtain a foam having high resilience and a lower wet

compression set. The wet compression set is a measure for the durability of a foam in humid conditions.

SUMMARY OF THE INVENTION

[0005] The present invention is directed to a formulation for preparing high resilience foam, which formulation comprises, based on total amount of polyol,

(i) 100 parts by weight of a polyol formulation comprising:

(a) a polymer-modified polyol formed by polymerizing an olamine with an organic polyisocyanate in the presence of a polyol;

(b) a polymer-modified polyol formed by polymerizing one or more ethylenically unsaturated monomers in the presence of a polyol; and,

(c) optionally further polyol

wherein the polyol present in polymer-modified polyol (a) and polymer-modified polyol (b) is prepared from hydroxyl containing starting compounds and is not an amine-based polyol;

(ii) 0.1 to 6 parts by weight of blowing agent;

(iii) 0.1 to 5 parts by weight of crosslinking agent(s);

(iv) 0.01 to 2.5 parts by weight of polyurethane catalyst(s); and optionally

(v) further usual auxiliaries.

[0006] The present invention is also directed to a process for preparing high resilience foam comprising combining a formulation as described above with isocyanate.

DETAILED DESCRIPTION OF THE INVENTION

[0007] The present invention uses a combination of (a) a polymer-modified polyol formed by polymerizing

an olamine with an organic polyisocyanate in the presence of a polyol and (b) a polymer-modified polymer formed by polymerizing one or more ethylenically unsaturated monomers in the presence of a polyol, wherein the polyol present in polymer-modified polyol (a) and polymer-modified polyol (b) is prepared from hydroxyl containing starting compounds and is not an amine-based polyol.

[0008] Organic polyisocyanates are organic isocyanates having two or more isocyanate groups. The organic polyisocyanates for polymerization with olamine may contain one or more different polyisocyanates. The polyisocyanate which may be used includes aliphatic, cycloaliphatic, aromatic and heterocyclic polyisocyanates. Of particular interest are the aromatic polyisocyanates, for example toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI) which are commercially available in substantially pure and crude forms. More particularly these include 2,4 and 2,6-toluene diisocyanates and mixtures thereof; diphenylmethane-2,4'-diisocyanates and mixtures thereof (generally referred to as pure MDI), for example, a mixture containing from 70 to 100%, especially 80%, by weight of the 4,4'-isomer and from 0 to 30%, especially 20%, by weight of the 2,4'-isomer; mixtures of MDI with polyphenyl polymethane polyisocyanates made by phosgenating a mixture of polyamines which is obtained by condensing aniline with formaldehyde (generally referred to as crude or polymeric MDI); and mixtures of TDI and MDI, pure or crude, for example, a mixture containing 60% by weight of TDI and 40% by weight of MDI. There may also be used diisocyanates which have been modified in known

manner to introduce a significant isocyanurate, carbodiimide, uretonimine, buiret or allophanate content. Other polyisocyanates which may be used include isocyanate-ended prepolymers, for example, reaction products of a diisocyanate with a deficiency of one or more low molecular weight polyols such as trimethylolpropane, dipropylene glycol or tripropylene glycol; and polyisothiocyanates, polyisoselenocyanates and mixtures thereof.

[0009] Olanines are defined as organic compounds having one or more hydroxyl groups and one or more amine groups, and may be any of those specified or described in GB-A-2,072,204, herein incorporated by reference. Suitable examples of olanines are: monoethanolamine, diethanolamine, triethanolamine, N-methylethanolamine, N-ethylethanolamine, N-butylethanolamine, N-methyldiethanolamine, N-ethyldiethanolamine, N-butyldiethanolamine, monoisopropanolamine, diisopropanolamine, triisopropanolamine, N-methylisopropanolamine, N-ethylisopropanolamine, N-propylisopropanolamine. Substituted alkanolamines may also be used. A preferred alkanolamine is triethanolamine.

[0010] The polymerization of the olamine with the organic polyisocyanate may be catalyzed using any of the conventional catalysts for polyurethane chemistry. Such catalysts include tertiary amines such as, for example, triethylenediamine, N-methylmorpholine, diethylethanolamine, and dimethylbenzylamine; tertiary phosphines such as trialkylphosphines, and dialkylbenzylphosphines; strong bases such as alkali and alkaline earth metal hydroxides, alkoxides and phenoxides; salts or organic acids such as sodium acetate, stannous

octoate, stannous oleate, lead octoate and zinc octoate; and organometallic derivatives such as disclosed in U.S. Patent No. 2,846,408, herein incorporated by reference. Further compounds known to be suitable to someone skilled in art, such as stabilizer, may be present during the polymerization. A preferred polymer is the condensation product of triethanolamine and toluene diisocyanate (TDI).

[0011] The polymer-modified polyol containing polymer formed by polymerizing olamine with an organic polyisocyanate, may contain of from 5 %wt to 50 %wt of polymer in polyol, more specifically of from 5 %wt to 20 %wt. Commercially available polymer-modified polyols suitable for use as polymer-modified polyol (a) are CARADOL® SP50-04 polymer polyol and DESMOPHEN® 7652 polymer polyol.

[0012] The polyol which is present in the polymer-modified polyol (a), the polymer-modified polyol (b) and the optional polyol (c) may be any polyol that is not an amine-based polyol known to be suitable to someone skilled in the art. Amine based polyols are polyols which are either initiated with a tertiary amine compound or contain a tertiary amine group in the polyol chain or are partially capped with a tertiary amine group. Amine based polyols are considered not to be present if less than 50 %wt of the polyol present is amine based polyol, more specifically less than 25 %wt, most specifically less than 2 %wt. The polyol present in (a) and the polyol present in (b) and optional polyol (c) may be the same or may be different. The nominal functionality of the polyol present in (a) and/or (b) and optional polyol (c) may vary widely. Usually, the polyol has a nominal average functionality of from 1 to 6. The

number average molecular weight of the polyol generally will be in the range of from 1000 to 13000, more specifically of from 2000 to 10,000, preferably of from 3000 to 7000. The primary hydroxyl content of the base polyol generally will be of from 0 % to 98 %, preferably of from 50 % to 95 %, most preferably of from 60 % to 95 %. The number average functionality preferably is of from 2.4 to 5, more specifically of from 2.5 to 4.5.

[0013] The polyol for use in (a), (b) and/or (c) generally may be a polyalkoxylated polyol. Polyoxy-alkylated polyols are prepared by reacting a hydroxyl containing compound with an alkylene oxide such as ethylene oxide, propylene oxide, butylene oxide and/or mixtures thereof. Preferably, the alkylene oxide is propylene oxide, optionally together with one or more other alkylene oxides like ethylene oxide or butylene oxide. Suitable hydroxyl containing starting compounds include polyfunctional alcohols, generally containing of from 2 to 8 hydroxyl groups. Examples of such alcohols comprise glycols, glycerol, pentaerythritol, trimethylolpropane, triethanolamine, sorbitol and mannitol. Usually a strong base like potassium hydroxide or a similar metal hydroxide salt is used as a catalyst in this type of reaction. However, catalysts such as double metal cyanide complex catalysts may also be used.

[0014] The polyol for use in the present invention may have been capped with poly(oxyethylene) moieties. This may be attained by adding ethylene oxide only at the end of the alkylene oxide, normally propylene oxide, polymerization reaction. This is also sometimes referred to as "tipping" with ethylene oxide. Tipping gives an increased primary hydroxyl

content such as a primary hydroxyl content of at least 50 %.

[0015] The polymer-modified polyol (b) is formed by polymerizing one or more ethylenically unsaturated monomers in the presence of polyol. The ethylenically unsaturated monomer for preparing the polymer is preferably chosen from the group consisting of vinyl aromatic hydrocarbons, like styrene and methyl styrene, acrylonitrile, methacrylonitrile, vinyl chloride, various alkyl acrylates and methacrylates, such as methyl methacrylate and t-butyl methacrylate, and conjugated dienes, like 1,3-butadiene and isoprene. Styrene, acrylonitrile and to a lesser extent (meth)acrylates are the most frequently used monomers, whereby polystyrene, poly(acrylonitrile), copolymers of styrene and acrylonitrile and terpolymers of styrene, acrylonitrile and methyl methacrylate are the polymers usually formed.

Preferably, the polymer-modified polyol (b) for use in the present invention comprises polymer formed by polymerizing styrene optionally in combination with acrylonitrile. The polymerization generally involves in-situ polymerizing one or more monomers via free radical polymerization. Such in-situ polymerization requires the presence of a free radical polymerization catalyst. If necessary, a dispersion stabilizing agent may also be present. Examples of polymer polyols containing this type of polymer are described in EP-A-0,76,491; EP-A-0,162,588; EP-A-0,343,907; US Patent No. 4,418,840 and EP-A-0,495,551, all of which are hereby incorporated by reference.

[0016] The dispersed polymer is generally present in polymer-modified polyol (b) in an amount of from 5 %

to 60% by weight based on total weight of polymer polyol, more specifically of from 5 %wt to 50 %wt. Examples of some commercially available polymer polyols which may be applied as polymer-modified polyol (b) include the polystyrene polyols CARADOL[®] MD25-02 and CARADOL[®] MD30-02 and the styrene-acrylonitrile polymer polyols CARADOL[®] MD22-40, CARADOL[®] MD22-02 and CARADOL[®] SP33-03.

[0017] The total amount of solid polymer particles present in the final polyol formulation preferably is of from 1 %wt to 25 %wt of solid polymer particles, more preferably of from 5 %wt to 20 %wt. In such polyol formulation, it is preferred that the formulation comprises of from 1 %wt to 15 %wt of polymer formed by polymerizing an olamine with an organic polyisocyanate and of from 1 %wt to 15 %wt of polymer formed by polymerizing one or more ethylenically unsaturated monomers. Preferably, the polyol formulation according to the present invention comprises the polymer-modified polyol (a) and the polymer-modified polyol (b) in such amount that the weight ratio of amount of polymer formed by polymerizing an olamine with an organic polyisocyanate to amount of polymer formed by polymerizing one or more ethylenically unsaturated monomers, is in the range of from 1 : 100 to 100 : 1, preferably of from 1 : 20 to 20 : 1, more preferably of from 1 : 10 to 10 : 1.

[0018] It has been found possible to reliably prepare high resilience foam having a relatively low compression set, more specifically a relatively low wet compression set, with the help of the above formulations. Therefore, the present invention further relates to the process of preparing high

resilience foam by reacting the above formulation with one or more polyisocyanates.

5 **[0019]** Water may be used as a (chemical) blowing agent by reacting with isocyanate groups according to the NCO/H₂O reaction, thereby releasing carbon dioxide which causes the blowing to occur. Other blowing agents, such as carbon dioxide and/or methylene chloride, may be used as well either per se or in combination with water. Preferably, water is the
10 blowing agent in the formulation according to the present invention.

[0020] Cross-linking agents useful in the present invention are polyfunctional alkanol amines. Preferred amines which may be included in the polyol
15 formulation to aid or maintain the miscibility of the first and second polyols include diethanolamine, often abbreviated as DEOA, triethanolamine, often abbreviated as TEOA, and glycerol. Most preferably, diethanolamine is used in the polyol formulation of
20 the present invention. Preferably, the crosslinking agent is present in an amount of from 0.1 to 5 parts by weight.

[0021] Polyurethane catalysts are known in the art and include many different compounds. An extensive
25 list of polyurethane catalysts is, for instance, given in US Patent No. 5,011,908, herein incorporated by reference. A preferred catalyst is an amine, especially a tertiary amine, catalyst. Preferred amine catalysts include an amine group substituted by
30 at least two optionally-substituted, preferably unsubstituted, lower alkyl groups which may be the same or different, but are preferably the same. A lower alkyl group may have up to 8, preferably up to 6, more preferably up to 4, carbon atoms, with methyl

and ethyl groups being especially preferred. A tertiary amine catalyst may be selected from bis(2,2'-dimethylamino)ethyl ether, trimethylamine, triethylamine, triethylenediamine, dimethyl-ethanolamine, N,N',N'-dimethylaminopropylhexahydrotriazine and N,N-dimethylcyclohexylamine. Examples of commercially available tertiary amine catalysts are those sold under the trademarks NIAX[®], TEGOAMIN[®], JEFFCAT[®] and DABCO[®]. Within the polyurethane catalysts and even within the tertiary amine catalysts a distinction may be made between gellation catalysts and blowing catalysts. Gellation catalysts are catalysts which predominantly promote the gellation of the foaming mixture, i.e. which promote the reaction between polyols and polyisocyanate. Typical gellation catalysts are stannous octoate and dibutyltindilaurate. Blowing catalysts predominantly promote the NCO/H₂O reaction, whereby carbon dioxide is released which causes the blowing to occur. Typical blowing catalysts are dimethylaminoethylether and urea.

[0022] Other usual auxiliaries may include fillers, flame retardants, foam stabilizers (surfactants) and colorants. The flame retardants may be liquid and/or solid flame retardants. Organosilicone surfactants are most conventionally applied as foam stabilizers in polyurethane production. A large variety of such organosilicone surfactants is commercially available. A preferred compound is compound L2100 commercially available from Osi. Usually, such foam stabilizer is used in an amount of up to 5% by weight based on the reaction mixture of polyol reactant and polyisocyanate reactant. The amount in which the usual auxiliaries may be present, may vary widely.

Generally, the amount will be of from 0 to 50 parts by weight, based on amount of polyol, more specifically of from 0 to 40 parts by weight.

5 **[0023]** The final foam is obtained by combining a formulation according to the present invention with isocyanate. Such process for preparing high resilience foam preferably comprises mixing the formulation according to the present invention with isocyanate at an isocyanate index of from 80 to 130,
10 more specifically of from 100 to 120. The isocyanate index is the relative amount of isocyanate used as compared with the theoretical requirement. The process is preferably carried out by intimately mixing all components but a polyisocyanate, then
15 adding the polyisocyanate and mixing this with the polyol formulation. The foams are subsequently allowed to form. The foam may be manufactured either batch-wise, or continuously such as with the help of a conveyor. Mixing of the various components is
20 preferably carried out at ambient temperature, suitably in the range of from 10 °C to 40 °C, preferably of from 20 °C to 25 °C.

[0024] Polyisocyanates that may be used are those conventionally applied in the production of
25 polyurethane foams. Useful polyisocyanates should contain at least two isocyanate groups and include both aliphatic (usually alkylene) and aromatic di-, tri-, tetra- and higher isocyanates known in the art to be suitably applied in the production of flexible
30 polyurethane foams. Mixtures of two or more of such aliphatic and/or aromatic polyisocyanates may also be applied. Examples of suitable polyisocyanates, include 2,4-toluene diisocyanate (2,4-TDI), 2,6-TDI, mixtures of 2,4-TDI and 2,6-TDI, 1,5-naphthene

diisocyanate, 2,4-methoxyphenyl diisocyanate, 4,4'-
diphenylmethane diisocyanate (MDI), 4,4'-biphenylene
diisocyanate, 3,3'-dimethoxy-4, 4'-biphenylene
diisocyanate, 3,3'-dimethyl-4, 4'-biphenylene
5 diisocyanate and 3,3'-dimethyl-4, 4'-diphenylmethane
diisocyanate, 4,4',4"-triphenylmethane triisocyanate,
2,4,6-toluene triisocyanate, 4,4'-dimethyl-2,2',5,5'-
diphenylmethane tetraisocyanate, polymethylene-
polyphenylene polyisocyanate, carbodiimide modified
10 isocyanates, MDI prepolymers and mixtures of two or
more of these. Polymeric MDI, a mixture of polyiso-
cyanates with MDI as the main component, may also be
used. For the purpose of the present invention the
use of TDI is preferred. Polyisocyanates are
15 commercially available.

[0025] An advantage of the present invention is that
a wide range of polyisocyanate indices may be used.
The polyisocyanate may be used in such amount that
the isocyanate index is in the range of from 80 to
20 130. Especially good results are obtained with
polyisocyanate indices in the range of from 85 to
120.

[0026] The density of the foam prepared with the
help of the present invention is relatively low.
25 Generally, the foam obtained will have a density of
at most 80 kg/m^3 , preferably at most 60 kg/m^3 . The
density preferably is at least 15 kg/m^3 , more
specifically at least 20 kg/m^3 .

[0027] The resilience of the foam is measured using
30 the standard ball rebound test (ASTM D 3574-95,
Test H). A preferred high resilience foam has the
property that the ball bounces back at least 20 %,
preferably at least 25 %, more preferably at least 30

%, more preferably at least 35 %, most preferably at least 40 %.

[0028] Other conventional ingredients used for making polyurethane foams may be incorporated into the formulation for preparing high resilience foam in accordance with the invention, such as surfactants, crosslinking or chain lengthening agents, additives to regulate cell size and structure, e.g. silicone oil or polysiloxane-polyalkylene oxide block copolymers, blowing agents, fillers, pigments, plasticizers and flame retardants, e.g. halogenated alkylphosphates and melamine. In relation to flame retardants it is possible that an olphosphine may be used in place of or in conjunction with an olamine in the preparation of the stabilizer and/or of the polymer-modified polyol, to confer flame retardation properties. Suitable olphosphines are discussed in detail in WO 92/02567; herein incorporated by reference.

[0029] The present invention is further illustrated in the Examples.

Examples

[0030] Polymer polyols, polyol and additives were mixed in different ratios.

PIPA polymer polyol

[0031] CARADOL[®] SP50-04 polymer polyol contains 10 %wt of the condensation product of triethanolamine and toluene diisocyanate (TDI) in a liquid polyol having a nominal functionality of 3 and a nominal average molecular weight of 4700 g/mole.

SAN polymer polyol

[0032] CARADOL[®] MD22-40 polymer polyol contains 40 %wt of a copolymer of styrene and acrylonitrile (molar ratio of styrene to acrylonitrile of about 0.7

to 0.8) in a liquid polyol having a nominal functionality of 3 and a nominal molecular weight of 4700 g/mole.

Polyol

5 **[0033]** CARADOL® MD36-13 is a liquid polyol having a nominal average functionality of 3 and a nominal molecular weight of 4700 g/mole.

10 **[0034]** With the exception of the isocyanate, the compounds described in Tables 1, 2 and 3 were blended into one stream. The isocyanate formed another stream. The amounts indicated as "php" are based on 100 parts by weight of polyols. Both streams were mixed and allowed to react.

15 **[0035]** The surfactant is L2100 silicone surfactant available from Osi.

20 **[0036]** CARADATE® T80 is a mixture of 80 % 2,4-toluene diisocyanate and 20 % 2,6- toluene diisocyanate.

25 **[0037]** The resilience was measured according to ASTM D 3574-95 Test H.

30 **[0038]** The compression sets were measured according ASTM D 3574-95 at 75% indentation. The dry compression set measurements were carried out at 70 °C for 22 hours, whereas the wet compression set measurements were performed in a humidity cabinet at 40 °C and 95% relative humidity for 22 hours.

35 **[0039]** The results of the foam evaluation are indicated in Tables 1 and 2.

40 **[0040]** The relatively high resilience and low wet compression set for foams according to the present invention, are clear from comparing the results obtained in the Comparative Examples with the results in the Examples which are according to the present invention. A lower compression set indicates a more durable foam.

TABLE 1

Formulation	Comparative Example 1A	Comparative Example 1B	Example 1
PIPA polymer polyol, pbw	100		28.3
SAN polymer polyol, pbw		20	12.7
Polyol, pbw		80	59
Water, php	1.6	1.6	1.6
Diethanolamine, php	0.2	1.4	1.4
Urea, php	0.11	0.11	0.11
L2100, php	0.4	0.4	0.4
Stannous octoate, php	0.15	0.15	0.15
Caradate T80, index	110	110	110
Properties			
Density, kg/m ³	51.3	51.7	50.2
Resilience, %	62	66	68
Dry compression set, %	2.8	2.4	2.4
Wet compression set, %	3.2	3.3	3.5

TABLE 2

Formulation	Comparative Example 2A	Comparative Example 2B	Example 2
PIPA polymer polyol, pbw	100		28.3
SAN polymer polyol, pbw		20	12.7
Polyol, pbw		80	59
Water, php	2.6	2.6	2.6
Diethanolamine, php	0.2	1.4	1.4
Urea, php	0.06	0.06	0.06
L2100, php	0.4	0.4	0.4
Stannous octoate, php	0.15	0.15	0.15
Caradate T80, index	110	110	110
Properties			
Density, kg/m ³	31.8	32.1	33.2
Resilience, %	55	59	63
Dry compression set, %	5.4	4.7	4.7
Wet compression set, %	11.9	12.2	9.7

TABLE 3

Formulation	Comp. 3A	Comp. 3B	Example 3
PIPA polymer polyol, pbw	100		28.3
SAN polymer polyol, pbw		20	12.7
Polyol, pbw		80	59
Water, php	3.6	3.6	3.6
Diethanolamine, php	0.2	1.4	1.4
Urea, php	0.06	0.06	0.06
L2100, php	0.4	0.4	0.4
Stannous octoate, php	0.15	0.15	0.15
Caradate T80, index	110	110	110
Properties			
Density, kg/m3	23.4	23.7	22.8
Resilience, %	49	54	52
Dry compression set,%	9.1	8	7.1
Wet compression set,%	27.3	27.4	21